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(54) Crosslinkable silyl polymer composition

(57) A granular composition capable of being crosslinked by the action of water in the presence of a silanol condensation catalyst comprises (A) a silyl polymer, (B) as a water scavenger, from 0.2 to 5.0 wt % of a hydrolysable unsaturated silane compound and, optionally, a silanol condensation catalyst. The composition exhibits a reduced tendency to undergo premature crosslinking during the fabrication of articles e.g. by extrusion.

The unsaturated silane may be ungrafted silane present after extruding a mixture of ethylene polymer and unsaturated silane to form a grafted ethylene polymer.

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SPECIFICATION

Polymer compositions and extrusion process

5 The present invention relates to crosslinkable organic polymer compositions. More particularly the present invention is concerned with crosslinkable compositions comprising organic polymers containing hydrolysable silane groups, which polymers can be thermoformed into shaped articles, for example cable insulation or pipe, and subsequently crosslinked by contacting the articles with water or steam in 10 the presence of a so-called "silanol condensation catalyst". The invention further relates to a process for extruding articles from crosslinkable compositions comprising such polymers. It is known that organic polymers containing 15 hydrolysable silane groups can be crosslinked by the action of water, preferably in the presence of a silanol condensation catalyst. A number of methods are known for producing such crosslinkable organic polymers.

20 25 One method comprises copolymerising unsaturated organic monomers, for example, ethylenically unsaturated or vinyl monomers, with unsaturated silane compounds containing hydrolysable groups. Examples of this method 30 are described in GB-A-2028831 and GB-A-2039513 which disclose the preparation of crosslinkable copolymers of ethylene and an ethylenically unsaturated silane compound by copolymerising the monomers at relatively 35 high temperatures and pressures in the presence of a radical polymerisation initiator. Another example of this copolymerisation method is described in GB-A-1415194 which discloses the preparation of crosslinkable co-40 polymer by contacting ethylene and a terminally unsaturated silane compound, optionally with other olefinically unsaturated comonomer, with certain defined Ziegler catalysts under polymerisation conditions which preferably employ relatively low temperatures and pressures.

45 It is also known that polymers crosslinkable by the action of water and silanol condensation catalyst can be prepared by grafting a 50 hydrolysable, unsaturated silane compound on to a preformed polymeric material. Grafting processes of this type can be carried out by heating together a base polymer, for example polyethylene, an unsaturated silane compound 55 bearing one or more hydrolysable groups, a grafting initiator and, optionally a silanol condensation catalyst, under conditions such that the hydrolysable, unsaturated silane compound is grafted on to the base polymer. Examples 60 of this method are disclosed in GB-A-1357549, GB-A-1234034 and GB-A- 65 1236460. An example of a commercial process which employs a grafting reaction of this type is the SIOPLAS (registered trade mark) process. In this process, the base polymer is

heated with the hydrolysable unsaturated silane in the presence of a grafting initiator and the product is extruded and pelleted to produce a pelleted silane-grafted thermoplastic 70 polymer. The pelleted polymer can then be fed with a silanol condensation catalyst to a thermoforming process for fabricating shaped products. These shaped products are then crosslinked by exposure to water or steam. 75 Other known methods for forming polymeric materials having hydrolysable silane groups include "transesterification" methods wherein a copolymer having exchangeable functions such as alkoxy groups (as, for example, in ethylene/ethyl acrylate copolymer) or carboxylate 80 groups (as, for example, in ethylene/vinyl acetate copolymer) is treated with a suitable silane compound in the presence of a special ester-exchange catalyst. In this method, for 85 example, the alkoxy groups present in an ethylene/alkyl(meth) acrylate copolymer can be "ester exchanged" or replaced by a silane substituent bearing hydrolysable groups by reacting the copolymer with a suitable silane 90 compound in the presence of a catalyst (for example, titanium tetrakisopropylate). Examples of suitable silane compounds are acetoxy propyl trimethoxy silane, acetoxy propyl triethoxy silane, methacryloxypropyl trimethoxy silane, 95 acryloxypropyl trimethoxy silane, methacryloxypropyl triethoxysilane and acryloxypropyl triethoxy silane. In another example of the transesterification method ethylene/vinyl acetate copolymer can be reacted with a suitable silane compound bearing hydrolysable groups and having esterified carboxylic acid groups which exchange with the acetate groups on the copolymer. A suitable silane compound is 100 4-[tri(m)ethoxysilyl] butanoic acid (m)ethyl ester. 105 Crosslinkable organic polymers having hydrolysable silane groups (hereinafter referred to as "silyl polymers") can be fabricated to form a large variety of useful articles by conventional techniques, for example, extrusion, injection moulding, blow-moulding and film-blown processes. The crosslinking step is generally carried out subsequent to fabrication of the article because the crosslinked polymer 110 115 cannot in general be satisfactorily thermoformed.

A problem encountered with silyl polymers is that during thermoforming operations the polymer can undergo premature crosslinking. 120 In addition, extrusion of blends of silyl polymer and a silanol condensation catalyst can result in "scorching" of the extruded product. "Scorching" is a term used in the art to describe the formation of surface imperfections 125 due to polymer which has crosslinked in the extruder before being deposited on the surface of the extrudate. Premature crosslinking, including "scorching" can lead to difficulties in the fabrication of products or the production 130 of articles having unsatisfactory physical and

mechanical properties. The problem can be particularly serious in the production of wire and cable insulation which should be well crosslinked, have good mechanical properties and low shrinkage. The insulation should also have a smooth surface since surface roughness can lead to electrical stress and insulation breakdown.

One method of reducing premature crosslinking proposed in GB-A-1357549 is to mould or extrude articles from silyl polymers in the absence of the silanol condensation catalyst and then to contact the produced article with an aqueous dispersion or solution of a tin carboxylate to cause the crosslinking. However, in many applications it is preferred to include the silanol condensation catalyst as a component of the polymer composition as this leads in general to higher crosslinking rates and to more complete crosslinking particularly in articles having thick cross section.

It is an object of the present invention to provide an improved composition comprising crosslinkable silyl polymer. It is a further object of the present invention to provide a crosslinkable silyl polymer composition which exhibits a reduced tendency to undergo premature crosslinking during the fabrication of articles therefrom.

Accordingly, one aspect of the present invention provides a granular composition capable of being crosslinked by the action of water in the presence of a silanol condensation catalyst, the composition comprising

(A) a silyl polymer and
 (B) as a water scavenger, from 0.2 to 5.0wt% of a hydrolysable unsaturated silane compound the wt% being based on the quantity of silyl polymer.

A further aspect of the present invention provides a granular composition capable of being crosslinked by the action of water comprising

(A) a silyl polymer,
 (B) as a water scavenger, from 0.2 to 5.0wt% of a hydrolysable unsaturated silane compound, the wt% being based on the quantity of silyl polymer, and
 (C) a silanol condensation catalyst.

The invention includes a process for producing an extruded article comprising feeding to an extruder a granular composition according to the present invention.

Also included is a process for producing an extruded article comprising feeding to an extruder, separately or together components comprising

(A) a silyl polymer
 (B) as a water scavenger, from 0.2 to 5.0 weight%, based on the weight of silyl polymer, of a hydrolysable unsaturated silane compound, and
 (C) a silanol condensation catalyst, to form an extruded article comprising a mixture of A, B and C.

The silyl polymer employed in the composition of the present invention is suitably any organic polymer containing hydrolysable silane groups which is crosslinkable by the action of water in the presence of a silanol condensation catalyst. Examples of such silyl polymers and references to their methods of manufacture are described above. Preferred silyl polymers are those prepared by copolymerising ethylene and an unsaturated silane compound having one or more hydrolysable groups, optionally together with one or more other monomers copolymerisable therewith, or those prepared by grafting a hydrolysable unsaturated silane compound on to a base polymer in the presence of a grafting initiator. Particularly preferred silyl polymers are those prepared by copolymerising ethylene and an unsaturated silane compound having one or more hydrolysable groups, optionally together with one or more other unsaturated compounds, at a temperature of 150 to 400°C and a pressure of 1000 to 4000 bar in the presence of a free radical polymerisation initiator. The hydrolysable, unsaturated silane compound employed in such processes is preferably a compound having the general formula $XSiX_1^nY_{3-n}$ wherein X represents an ethylenically unsaturated hydrocarbyl or hydrocarboxy group; X^1 represents an aliphatic saturated hydrocarbyl group; Y represents a hydrolysable organic group; and n represents zero, 1 or 2. X can be, for example, vinyl, allyl, isopropenyl, butenyl, cyclohexenyl or gamma-methacryloxypropyl. Y can be, for example, methoxy, ethoxy, formyloxy, acetoxy, propionyloxy, alkylamino or arylamino. X^1 can be, for example, methyl, ethyl, propyl, hexyl, octyl, decyl or phenyl. X is preferably a vinyl group, Y is preferably methoxy, ethoxy or acetoxy. Preferred hydrolysable, unsaturated silane compounds for use in such processes for forming silyl polymers are vinyl trimethoxy silane, vinyl triethoxy silane and vinyl triacetoxy silane.

The silyl polymer suitably contains 0.1–10 weight %, preferably 0.5 to 5 weight % of copolymerised or grafted units of the hydrolysable unsaturated silane compound (based on silyl polymer).

Whilst it will be appreciated that commercial silyl polymers (for example copolymers of ethylene and vinyl trimethoxy silane or polyethylene having grafted-on hydrolysable silane units) may contain small quantities of residual unreacted unsaturated silane compound, the quantity of unsaturated silane present in the crosslinkable granular composition of the present invention is substantially in excess of such residual quantities.

The water scavenger employed in the composition of the present invention is suitably a compound having the general formula $ZSiZ_1^nQ_{3-m}$ wherein Z represents an ethylenically unsaturated hydrocarbyl or hydrocarby-

loxy group; Z' represents an aliphatic saturated hydrocarbyl group; Q represents a hydrolysable organic group; and m represents zero, 1 or 2. Z can be, for example, vinyl, 5 allyl, isopropenyl, butenyl, cyclohexenyl or gamma-methacryloxy propyl. Z' can be, for example, methyl, ethyl, propyl, hexyl, octyl, decyl or phenyl. Q can be, for example, methoxy, ethoxy, formyloxy, acetoxy, propionyloxy, alkylamino or arylamino. Preferred unsaturated silane compounds for use as the water scavenger are vinyl trimethoxy silane, 10 vinyl triethoxy silane and vinyl triacetoxyl silane.

15 The quantity of unsaturated silane employed as water scavenger in the composition of the present invention is preferably 0.2 to 4.0 weight %, most preferably 0.5 to 3.0 weight% based on the weight of the silyl polymer.

20 The silanol condensation catalyst can be present in the granular composition of the present invention or can be employed by application direct to articles formed from the composition of the present invention. It is preferred to include the silanol condensation catalyst in the composition.

25 Any of the silanol condensation catalysts known in the art for crosslinking silyl polymers can be suitably employed in the present invention. Examples of suitable classes of silanol condensation catalysts are organic and inorganic acids and alkalis, and metal compounds, for example complexes or carboxylates of 30 lead, cobalt, iron, nickel, zinc and tin. Specific examples of the silanol condensation catalyst are dibutyl tin dilaurate, dibutyl tin diacetate, dibutyl tin dioctoate, stannous acetate, stannous caprylate, lead naphthenate, zinc caprylate, cobalt naphthenate; ethylamines, dibutylamine, hexylamines, pyridine; inorganic acids such as sulfuric acid and hydrochloric acid; and organic acids such as toluenesulfonic acid, 35 acetic acid, stearic acid and maleic acid. Carboxylates of tin are preferred. Particularly preferred silanol condensation catalysts are dialkyl tin carboxylates, for example dibutyl tin dilaurate, dibutyl tin dipalmitate, dibutyl tin distearate, dioctyl tin dilaurate and dibutyl tin maleate.

40 The quantity of silanol condensation catalyst employed in the granular crosslinkable composition of the present invention or applied direct to articles formed from the composition is suitably in the range 0.001 to 3.0 moles, 45 preferably in the range 0.003 to 0.05 moles per mole of silyl units in the silyl polymer.

50 Generally speaking, the quantity of the silanol condensation catalyst is in the range of 0.001 to 10% by weight, preferably 0.01 and 55 5% by weight, most preferably 0.03 to 3% by weight, relative to the quantity of silyl polymer in the composition.

60 It is preferred to prepare the granular composition of the present invention as a homo-

geneous dispersion of the unsaturated silane water scavenger in the silane polymer granules. However, heterogeneous mixtures can be prepared if desired.

65 The granular composition of the present invention comprising the silyl polymer and the water scavenger, optionally with a silanol condensation catalyst and/or any other ingredients of the composition, can be prepared by a variety of techniques including, for example, direct blending or compounding of the ingredients, or by the use of masterbatch techniques.

70 The composition can be prepared for example by contacting the silyl polymer in granular form (e.g. powder or pellets) with the water scavenger under conditions such that the water scavenger is absorbed by the polymer granules. If desired, other additives, for example the silanol condensation catalyst and/or antioxidant can be absorbed into the polymer using the same type of absorption technique. Thus, if desired, the granular polymer can be tumbled with a mixture of water 75 scavenger, silanol condensation catalyst and antioxidant until absorption of the ingredients is substantially complete. The rate of absorption can be increased by the use of elevated temperatures and/or intensive mixing if desired.

80 In another method of making the composition of the present invention, the silyl polymer can be melted in the presence of the water scavenger and optionally in the presence of any other desired ingredients. Such melting is preferably carried out in an extruder or in proprietary compounding apparatus, e.g. a Banbury mixer.

85 In a further method of making the composition of the present invention, the water scavenger and optionally any other ingredients which it is desired to incorporate in the composition, can be included in a granular masterbatch, prior to compounding the masterbatch 90 with the granular silyl polymer.

95 In the case that the silyl polymer is prepared by grafting an unsaturated silane on to a base polymer, for example low density polyethylene, linear low density polyethylene, ethylene/ethyl acrylate copolymer or ethylene/vinyl acetate copolymer, the water scavenger can for example be incorporated by employing an excess quantity of unsaturated silane in relation to the quantity which grafts on to the 100 base polymer. Under these circumstances the excess of silane remaining in the silane-grafted polymer acts as water scavenger. The quantity of silane which grafts to the base polymer can be readily controlled, for example by controlling the relative quantities of free radical initiator and unsaturated silane, by controlling the temperature and/or duration of the grafting reaction or by adding a reagent known to inactivate the initiator when the desired level 105 of grafting has been obtained. The compo-

sition is then granulated (e.g. pelleted) for storage or further use prior to or during the performance of the grafting reaction.

A crosslinkable composition according to 5 the present invention comprising the silyl polymer, the water scavenger, optionally a silanol condensation catalyst and, optionally other ingredients, can for example be prepared directly in the form of crosslinkable finished articles by extruding a base polymer, e.g. a homopolymer or copolymer of ethylene, together with the water scavenger, a hydrolysable, unsaturated silane compound of the type described earlier in this specification, a free radical catalyst for grafting (e.g. an organic peroxide) and a silanol condensation catalyst.

The granular composition of the present invention can contain additives conventionally employed in the art. Examples of such additives are antioxidants, fillers, metal deactivators (e.g. salicylaldehyde oxime), lubricants, water-tree inhibitors, foaming agents, flame retardants and pigments. Additives of this type are conventionally incorporated into the composition either directly or by a masterbatching technique. The additives can, if desired, be treated with the unsaturated silane water scavenger compound prior to their incorporation in the composition of the present invention. 30 For example, a flame retardant composition in accordance with the present invention can be made by treating aluminium trihydrate with the water scavenger, and then blending the product with the silyl polymer and any other desired ingredients of the composition. The composition can also be blended with other compatible polymeric materials, for example, polyethylene, polypropylene, ethylene/ethyl acrylate copolymer and ethylene/1-olefin co-polymer (e.g. LLDPE).

The composition of the present invention can be used to manufacture crosslinked products using the technology known in the manufacture of articles from conventional silyl polymers. For example, the composition can be used in blow-moulding, injection-moulding, film-blowing, calendering, extrusion, rotomoulding and extrusion-coating techniques. The composition is particularly preferred for 50 wire and cable coating applications. Wire and cable insulation produced by extrusion coating using the composition of the present invention exhibits improved surface finish.

Articles fabricated from the composition of 55 the present invention can be readily crosslinked by exposure to water. For example, the crosslinking can be effected by simply storing the fabricated articles under ambient conditions of temperature and humidity for a sufficient length of time, by storing in a humid atmosphere or by treating the articles with water or steam e.g. the articles can be passed through a water bath, sprayed with water or stored in a steam filled cabinet.

CLAIMS

1. A granular composition capable of being crosslinked by the action of water in the presence of a silanol condensation catalyst, the composition comprising;
 - (A) a silyl polymer and
 - (B) as a water scavenger, from 0.2 to 5.0 wt % of a hydrolysable, unsaturated silane compound, the wt % being based on the quantity of silyl polymer
2. A granular composition capable of being crosslinked by the action of water comprising;
 - (A) a silyl polymer,
 - (B) as a water scavenger, from 0.2 to 5.0 wt % of a hydrolysable, unsaturated silane compound, the wt % being based on the quantity of silyl polymer and
 - (C) a silanol condensation catalyst
3. A granular composition as claimed in either claim 1 or claim 2 in which the silyl polymer is a copolymer prepared by copolymerising ethylene and an unsaturated silane group having one or more hydrolysable groups.
4. A granular composition as claimed in any one of claims 1 to 3 in which the water scavenger is a compound having the general formula $ZSiZ^{1.m}Q_{3.m}$ in which Z represents an ethylenically unsaturated hydrocarbyl or hydrocarboxy group; Z^1 represents an aliphatic saturated hydrocarbyl group; Q represents a hydrolysable organic group; and m represents zero, 1 or 2.
5. A granular composition as claimed in claim 4 in which the water scavenger is selected from the group comprising vinyl trimethoxy silane, vinyl triethoxy silane and vinyl triacetoxy silane.
6. A granular composition as claimed in any one of claims 1 to 5 in which the amount of the water scavenger is from 0.5 to 3.0 weight %, based on the weight of silyl polymer.
7. A process for producing an extruded article comprising feeding to an extruder a granular composition as claimed in any one of claims 1 to 6.
8. A process for producing an extruded article comprising feeding to an extruder, separately or together,
 - (A) a silyl polymer and
 - (B) as a water scavenger, from 0.2 to 5.0 wt % of a hydrolysable, unsaturated silane compound, the wt % being based on the quantity of silyl polymer and
 - (C) a silanol condensation catalyst and forming an extruded article comprising a mixture of A, B and C.
9. A process for producing an extruded article comprising feeding to an extruder;
 - (A) a homopolymer or copolymer of ethylene
 - (B) a hydrolysable unsaturated silane compound
 - (C) a free radical catalyst and

(D) a silanol condensation catalyst extruding the mixture to form an extruded article under such conditions that part of the hydrolysable unsaturated silane compound is grafted to the homopolymer or copolymer of ethylene and leaving ungrafted from 0.2 to 5.0 wt % of the hydrolysable unsaturated silane compound, the weight % being based on the quantity of grafted silyl polymer.

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